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**WO 01/24983 A1**

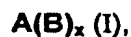
(54) Title: **PROCESS FOR PIGMENTING WOOD**

(57) Abstract: A process for pigmenting wood, which comprises treating wood in succession: a) with a solution comprising from 0.01 to 80 % by weight, based on the solution, of a compound of the formula:  $A(B)_x$  (I), in which x is an integer from 1 to 8, and from 0.05 to 5 % by weight, based on the solution, of a salt of the formula:  $Kat^+An^-$  (II),  $Kat^+.1/2An^{2-}$  (III) or  $Kat^+.1/3An^{3-}$  (IV), in which  $Kat^+$  is lithium, sodium, potassium or ammonium,  $An^-$  is formate, acetate, propionate or hydrogen carbonate,  $An^{2-}$  is oxalate, maleate, fumarate, malonate, carbonate or hydrogen phosphate, and  $An^{3-}$  is citrate or phosphate, in water or an organic solvent or in a single-phase mixture thereof, b) with a solution comprising from 0.01 to 50 % by weight, based on the solution, of an organic  $C_1-C_6$  carboxylic acid in water or an organic solvent or in a single-phase mixture thereof, and c) converting the compound of the formula (I) thermally to a pigment of the formula  $A(H)_x$  (V).

The invention therefore relates to a process for pigmenting wood, which comprises treating wood in succession

a) with a solution comprising

- from 0.01 to 80% by weight, based on the solution, of a compound of the formula



in which x is an integer from 1 to 8,

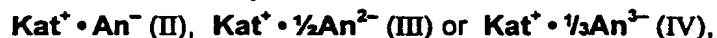
A is the radical of a chromophore of the quinacridone, anthraquinone, perylene, indigo, quinophthalone, indanthrone, isoindolinone, isoindoline, dioxazine, azo, phthalocyanine or diketopyrrolopyrrole series which is attached to x groups B via one or more heteroatoms, these heteroatoms being selected from the group consisting of N, O and S and forming part of the radical A,

B is hydrogen or a group of the formula  $\text{—}\overset{\text{O}}{\parallel}\text{—O—L}$ , at least one group B not being hydrogen and, if x is a number from 2 to 8, the groups B being identical or different, and

L is any desired group suitable for solubilization;

and

- from 0.05 to 5% by weight, based on the solution, of a salt of the formula



in which  $\text{Kat}^+$  is lithium, sodium, potassium or ammonium,  $\text{An}^-$  is formate, acetate, propionate or hydrogen carbonate,  $\text{An}^{2-}$  is oxalate, maleate, fumarate, malonate, carbonate or hydrogen phosphate, and  $\text{An}^{3-}$  is citrate or phosphate,

in water or an organic solvent or in a single-phase mixture thereof,

b) with a solution comprising from 0.01 to 50% by weight, based on the solution, of an organic  $\text{C}_1\text{--C}_6$  carboxylic acid in water or an organic solvent or in a single-phase mixture thereof, and

c) converting the compound of the formula (I) thermally to a pigment of the formula  $\text{A(H)}_x$  (V).

Process for pigmenting wood

The background of the invention is constituted by composite wood materials which are to be processed only after colouring. Thin sheets of wood, coloured right through, are bonded together, shaped and then cut at a wide variety of angles to produce artistic effects which depend on the grain. These materials may be used in particular to produce design articles or for decorative purposes. The requirements in terms of light stability and right-through coloration are therefore significantly higher than in the case of customary wood veneers. In particular, it is essential for the individual sheets of wood to be coloured right through with a high degree of homogeneity, even in the case of relatively great thicknesses, since the core of the sheets becomes visible as a result of the artistic cutting.

JP-A-54/113403 discloses a process for the homogeneous colouring of wood veneers, in which the wood is first treated under hot conditions with an alkali, including sodium acetate and sodium bicarbonate, at a pH of 10 and only then is coloured with an appropriate dye, for example with C.I. Acid Blue 171.

JP-A-61/41503 discloses a process for the homogeneous colouring of wood veneers with an anionic direct dye, the optimum being achieved using a moderately soluble salt, including sodium bicarbonate, in saturated concentration.

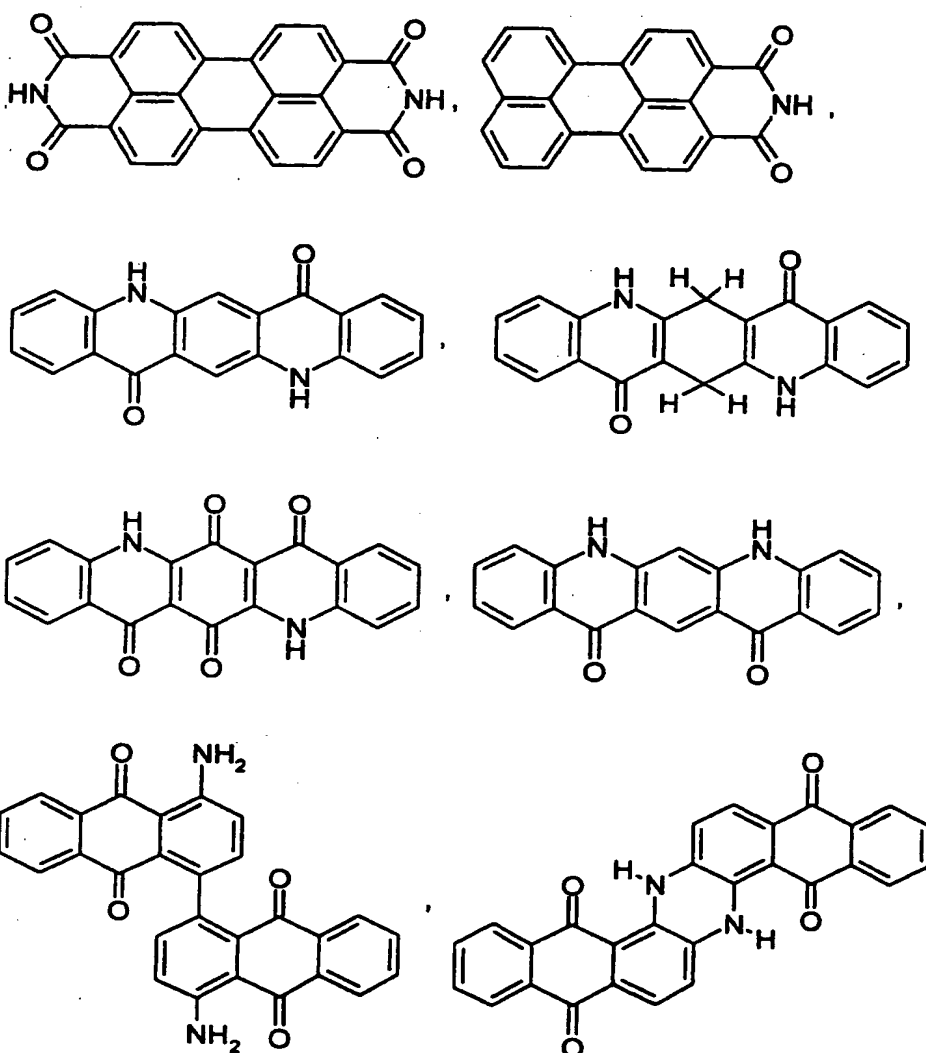
However, these dyes do not have sufficiently satisfactory fastness properties for the abovementioned applications, especially when used outdoors or when exposed to sunlight, for example as wall boards in a glazed corridor.

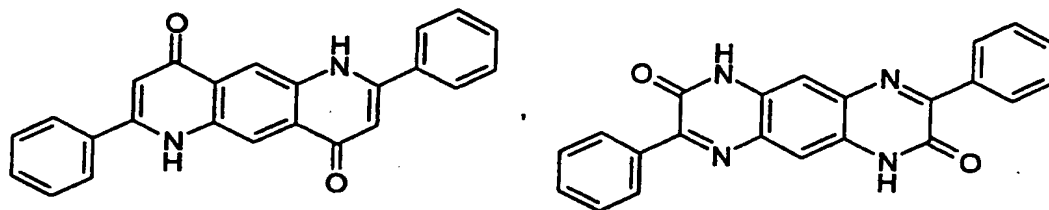
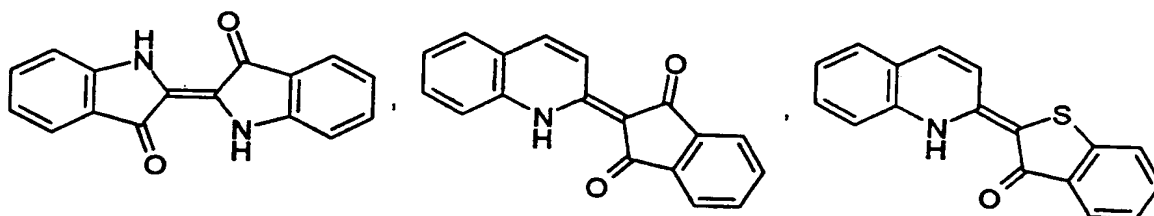
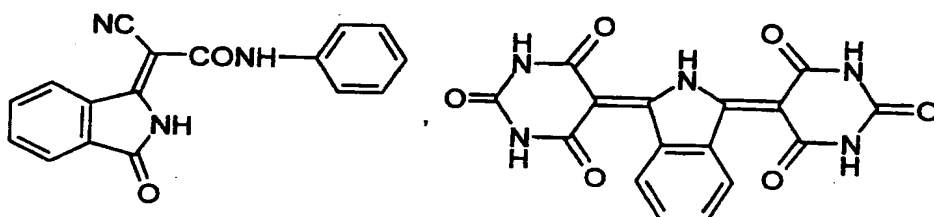
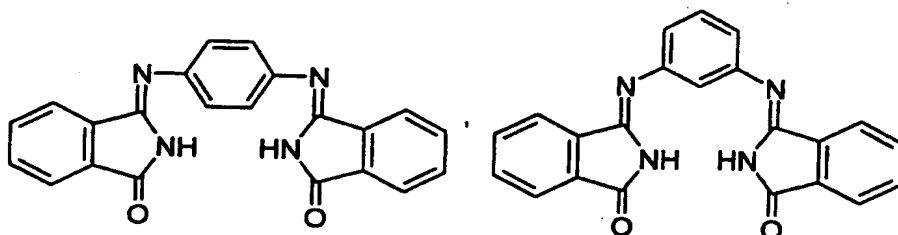
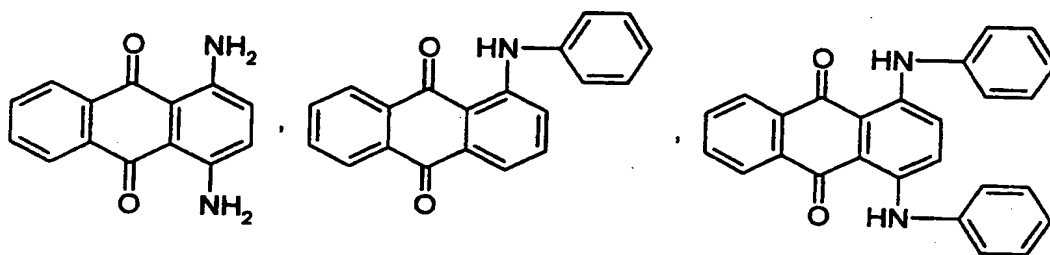
WO-98/58027 discloses the colouring of porous materials, including wood, starting from soluble pigment precursors. However, the pigmentation is greater at the surface than in the interior of the material. It has been found, moreover, that the presence of an acid is necessary as a catalyst for regenerating the majority of pigments, to ensure that the pigment is not damaged by overheating to 160°C or more.

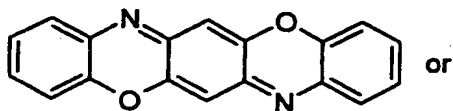
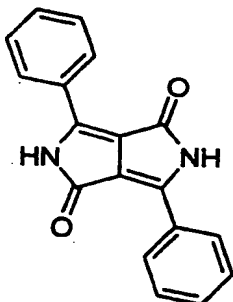
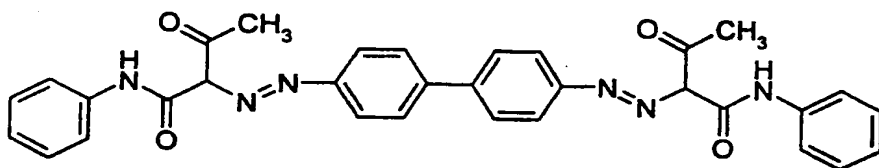
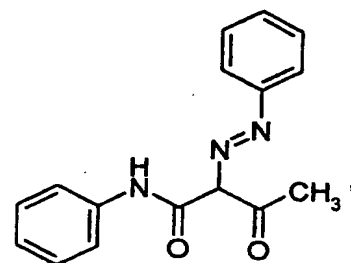
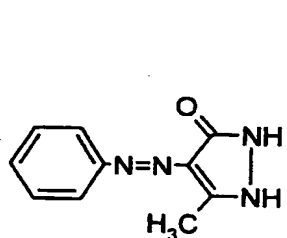
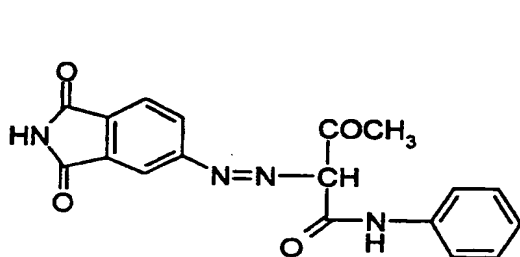
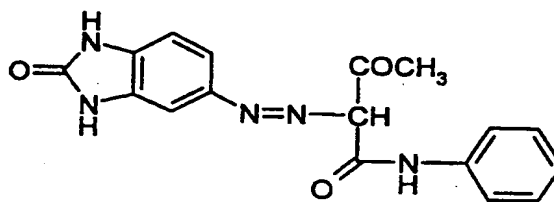
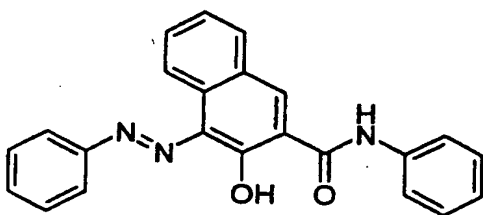
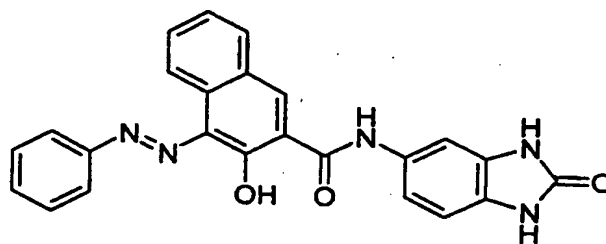
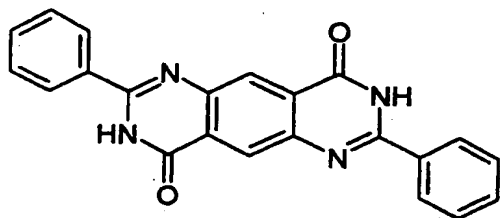
It has now surprisingly been found that pigmentation of wood materials with significantly better penetration is obtained if wood is treated in succession with soluble pigment precursors from WO-98/58027 in the presence of a small amount of a weakly basic salt and subsequently with an organic acid, and only then is the pigment thermally regenerated.

The wood in question may be any desired hardwood or softwood, such as obeche, ash, birch, poplar, fir, spruce, pine, tulip tree, maple, bird's-eye maple, sycamore maple, oak, beech, mahogany, myrtle, anigre, tay (koto), mappa, elm, zebrano, carbalho, vavona or ogea, for example.

A is the radical of known chromophores having the basic structure  $A(H)_x$  (VI), A preferably having at least one directly adjacent or conjugated carbonyl group on each heteroatom attached to x groups B, such as







$L_1$  and  $L_2$  independently of one another are  $[-(p',q'-C_2-C_6\text{alkylene})-Z-]_n-C_1-C_6\text{alkyl}$  or  $C_1-C_6\text{alkyl}$  which is unsubstituted or substituted one or more times by  $C_1-C_{12}\text{alkoxy}$ ,  $C_1-C_{12}\text{alkylthio}$ ,  $C_2-C_{24}\text{dialkylamino}$ ,  $C_6-C_{12}\text{aryloxy}$ ,  $C_6-C_{12}\text{arylthio}$ ,  $C_7-C_{24}\text{alkylaryl amino}$  or  $C_{12}-C_{24}\text{diaryl amino}$ ,  $n$  being a number from 1 to 1000,  $p'$  and  $q'$  being different locants, each  $Z$  independently of the others being a heteroatom O, S or  $C_1-C_{12}\text{alkyl-substituted N}$ , and  $C_2-C_6\text{alkylene}$  in the repeating units  $[-C_2-C_6\text{alkylene}-Z-]$  being identical or different,

and  $L_1$  and  $L_2$  may be saturated or unsaturated 1 to 10 times, uninterrupted or interrupted at any desired points by from 1 to 10 groups selected from the group consisting of  $-(C=O)-$  and  $-C_6H_4-$ , and  $L_1$  and  $L_2$  may carry none or from 1 to 10 further substituents selected from the group consisting of halogen, cyano and nitro.

Of particular interest are compounds of the formula (I), in which  $L$  is  $C_1-C_6\text{alkyl}$ ,  $C_2-C_6\text{alkenyl}$

or  $-(L_2)_m - Q - X - L_1$ , in which  $Q$  is  $C_2-C_4\text{alkylene}$ , and

$L_1$  and  $L_2$  are  $[-C_2-C_{12}\text{alkylene}-Z-]_n-C_1-C_{12}\text{alkyl}$  or are  $C_1-C_{12}\text{alkyl}$  substituted one or more times by  $C_1-C_{12}\text{alkoxy}$ ,  $C_1-C_{12}\text{alkylthio}$  or  $C_2-C_{24}\text{dialkylamino}$ , and  $m$  and  $n$  are as defined above.

Of very particular interest are compounds of the formula (I) in which  $L$  is  $C_4-C_5\text{alkyl}$ ,

$C_3-C_6\text{alkenyl}$  or  $-(L_2)_m - Q - X - L_1$ , in which  $Q$  is  $C_2-C_4\text{alkylene}$ ,  $X$  is O and  $m$  is zero, and  $L_1$  is  $[-C_2-C_{12}\text{alkylene}-O-]_n-C_1-C_{12}\text{alkyl}$  or is  $C_1-C_{12}\text{alkyl}$  substituted one or more times by  $C_1-C_{12}\text{alkoxy}$ , especially those in which  $-Q-X-$  is a group of the formula  $-C(CH_3)_2-CH_2-O-$ .

Alkyl or alkylene may be straight-chain or branched, monocyclic or polycyclic.

$C_1-C_{12}\text{Alkyl}$  is therefore, for example, methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, *tert*-butyl, cyclobutyl, *n*-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, cyclopentyl, cyclohexyl, *n*-hexyl, *n*-octyl, 1,1,3,3-tetramethylbutyl, 2-ethylhexyl, nonyl, trimethylcyclohexyl, decyl, menthyl, thujyl, bornyl, 1-adamantyl, 2-adamantyl or dodecyl.

If  $C_2-C_{12}\text{alkyl}$  is mono- or polyunsaturated, it is  $C_2-C_{12}\text{alkenyl}$ ,  $C_2-C_{12}\text{alkynyl}$ ,  $C_2-C_{12}\text{alkapolyenyl}$  or  $C_2-C_{12}\text{alkapolyynyl}$ , it being possible for two or more double bonds to be present, if desired, in isolation or conjugation, such as vinyl, allyl, 2-propen-2-yl, 2-buten-

preference from 80 to 120°C.

The concentration of the organic C<sub>1</sub>-C<sub>8</sub>carboxylic acid is preferably from 0.1 to 20% by weight, based on the solution.

The conversion of the pigment precursor to its pigmentary form takes place by fragmentation under known conditions, for example thermally, in the presence or absence of an additional catalyst, for example a cationic photoinitiator, which may be introduced before, simultaneously with or after the pigment precursor into the pores of the porous material. If desired, use is made preferably of the catalysts described in EP-99810107.5.

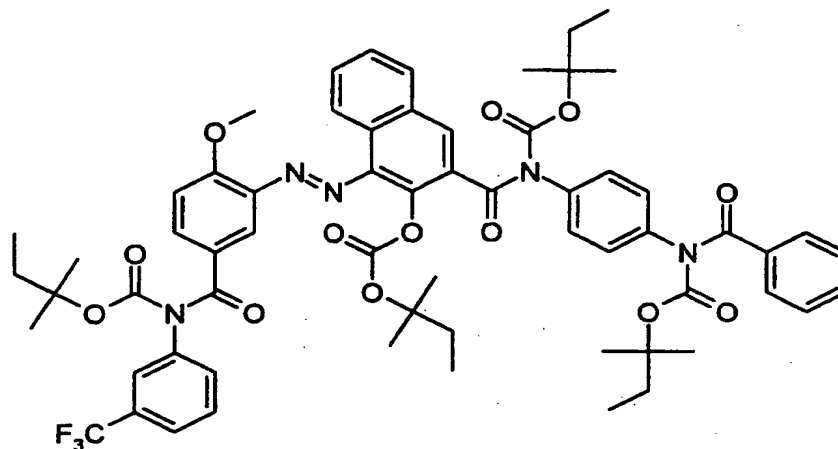
Fragmentation may be carried out individually, or simultaneously with any subsequent known further treatment, for example during curing of an additional transparent coating film.

Heating may be effected by any desired means, for example by treatment in a thermal oven or by electromagnetic radiation, for example IR or NIR radiation, or microwaves, in the presence or absence of a catalyst. The conditions required for fragmentation are known per se for each class of pigment precursor.

The temperature for converting the soluble pigment precursors to the corresponding pigments is judiciously from 40 to 160°C. It is preferably from 60 to 140°C, with particular preference from 80 to 120°C. The examples which follow illustrate the invention without restricting its scope (unless stated otherwise, "%" is always % by weight):

**Example 1:** In a 1.5 l reaction vessel provided with a stirrer, a thermometer and a nitrogen inlet, 50.0 g of Pigment Red 222 are suspended in 500 ml of o-xylene. At room temperature, 4.4 g of dimethylaminopyridine and 88.7 g of di-t-amyl pyrocarbonate are added. The reaction mixture is stirred at 23°C for 16 hours. Subsequently, the solution is concentrated to a third of its volume under reduced pressure at 40°C and then 60 ml of ethanol are added. 600 ml of n-hexane are added dropwise with rapid stirring. The precipitated product is filtered off, washed with hexane and dried at 40°C/20 mbar. This gives 80.7 g (98% of theory) of an outstandingly pure, bright red powder of the structure:





The  $^1\text{H-NMR}$ , TGA and C,N,H,F analytical data are in agreement with the structure. The purity (determined by HPLC) is 99%.

**Example 2:** A piece of obeche wood measuring  $50 \times 50 \times 0.6$  mm is immersed at  $100^\circ\text{C}$  for 16 hours in a solution of 3.0 g of compound from Example 1 and 0.2 g of  $\text{NaHCO}_3$  in 92 g of Dowanol<sup>®</sup> 33-B (1-methoxy-2-propanol) and 5 g of water. After the coloration, the wood is removed, predried in air for 45 minutes and then dried at  $80^\circ\text{C}/150$  mbar for 15 minutes. It is then immersed for 2 hours in a solution of 5 g of citric acid in 95 ml of water and subsequently dried at  $140^\circ\text{C}$  for 30 minutes. Visual inspection on a transverse cut shows homogeneous coloration right through.

**Example 3:** The procedure of Example 2 is repeated but using 0.1 g of sodium acetate, 87 g of Dowanol<sup>®</sup> 33-B and 10 g of water. The results are the same as those of Example 2.

**Example 4:** A piece of bleached obeche wood measuring  $110 \times 32 \times 0.8$  mm is immersed at  $110^\circ\text{C}$  for 6 hours in a solution of 0.08 g of the compound from Example 1 and 0.1 g of  $\text{NaHCO}_3$  in 85 g of Dowanol<sup>®</sup> 33-B and 15 g of water. The closed vessel is rotated. Following the coloration, the wood is removed and treated further as in Example 2. Visual inspection on a transverse cut shows homogeneous coloration right through.

**Example 5:** The procedure of Example 4 is repeated but using  $\text{Na}_2\text{CO}_3$  instead of  $\text{NaHCO}_3$ . The results are comparable with those of Example 4.

**Examples 6-14:** The procedure of Example 4 is repeated but replacing 0.1 g of  $\text{NaHCO}_3$  by

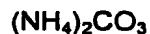
0.15 g of each of the following salts:



tri-potassium citrate



sodium formate



tri-sodium citrate

potassium formate

The results are in all cases good and comparable with those of Example 4, especially as regards colouring right through.

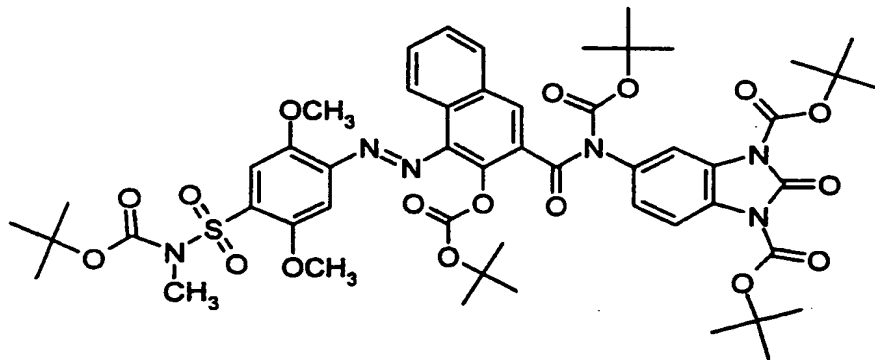
Example 15: The procedure of Example 4 is repeated but using 0.25 g of  $\text{CaCO}_3$  instead of 0.1 g of  $\text{NaHCO}_3$ .

Examples 16-27: The procedure of Examples 4-15 is repeated but replacing the compound from Example 1 by the compound from Example A4 of WO-00/36210 or Example 5 of WO-00/39221. The results are analogous to those of Examples 4-15.

Examples 28-39: The procedure of Examples 4-15 is repeated but replacing the compound from Example 1 by the compound from Example A2 of WO-00/36210 (STN Registry Number 214289-84-6). The results are analogous to those of Examples 4-15.

Examples 40-51: The procedure of Examples 28-39 is repeated but replacing the compound from Example 1 by the compound from Example A8 of WO-00/36210. The results are analogous to those of Examples 28-39.

Examples 52-63: The procedure of Examples 4-15 is repeated but replacing the compound from Example 1 by the compound of the following structure (obtainable in accordance with methods known per se from C.I. Pigment Violet 32):

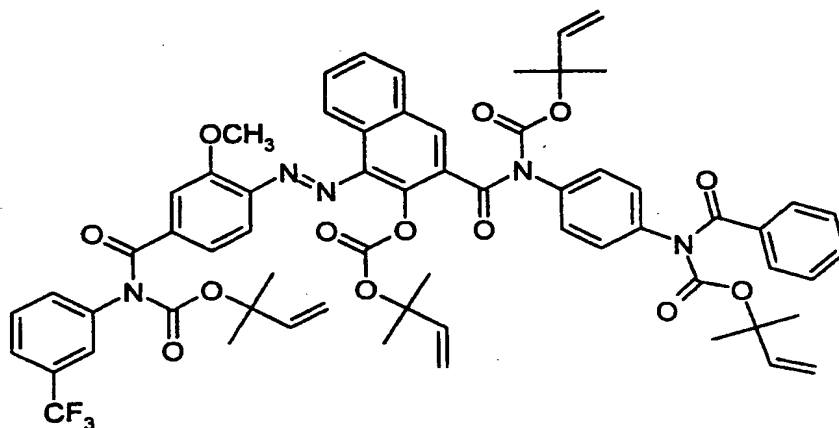


The results are analogous to those of Examples 4-15.

Examples 64-75: The procedure of Examples 4-15 is repeated but replacing the compound from Example 1 by the compound from Example 15 of WO-98/32802. The results are analogous to those of Examples 4-15.

Examples 76-87: The procedure of Examples 4-15 is repeated but replacing the compound from Example 1 by the compound from Example 11 of PCT/EP-00/03085. The results are analogous to those of Examples 4-15.

Examples 88-99: The procedure of Examples 4-15 is repeated but replacing the compound from Example 1 by the compound of the following structure (obtainable in accordance with the method known from US-6,063,924 from C.I. Pigment Red 222):



The results are analogous to those of Examples 4-15.

Examples 100-111: The procedure of Examples 4-15 is repeated but replacing the compound from Example 1 by the compound from Example B1 of EP-A-1 044 945. The results are analogous to those of Examples 4-15.

Examples 112-123: The procedure of Examples 4-15 is repeated but replacing the compound from Example 1 by the compound from Example A4 of WO-00/36210 (STN Registry Number 214289-82-4). The results are analogous to those of Examples 4-15.

Examples 124-243: The procedure of Examples 4-123 is repeated but using 3 g each of

soluble pigment precursor and compound of the formula (II), (III) or (IV).

Examples 244-263: The procedure of Examples 4-123 is repeated but using the soluble pigment precursor in saturated concentration and using in each case 1 g of the compound of the formula (II), (III) or (IV).

## WHAT IS CLAIMED IS:

1. A process for pigmenting wood, which comprises treating wood in succession:

a) with a solution comprising

- from 0.01 to 80% by weight, based on the solution, of a compound of the formula



in which x is an integer from 1 to 8,

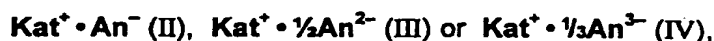
A is the radical of a chromophore of the quinacridone, anthraquinone, perylene, indigo, quinophthalone, indanthrone, isoindolinone, isoindoline, dioxazine, azo, phthalocyanine or diketopyrrolopyrrole series which is attached to x groups B via one or more heteroatoms, these heteroatoms being selected from the group consisting of N, O and S and forming part of the radical A,

B is hydrogen or a group of the formula  $\text{—}\overset{\text{O}}{\parallel}\text{—O—L}$ , at least one group B not being hydrogen and, if x is a number from 2 to 8, the groups B being identical or different, and

L is any desired group suitable for solubilization;

and

- from 0.05 to 5% by weight, based on the solution, of a salt of the formula



in which  $\text{Kat}^+$  is lithium, sodium, potassium or ammonium,  $\text{An}^-$  is formate, acetate, propionate or hydrogen carbonate,  $\text{An}^{2-}$  is oxalate, maleate, fumarate, malonate, carbonate or hydrogen phosphate, and  $\text{An}^{3-}$  is citrate or phosphate,

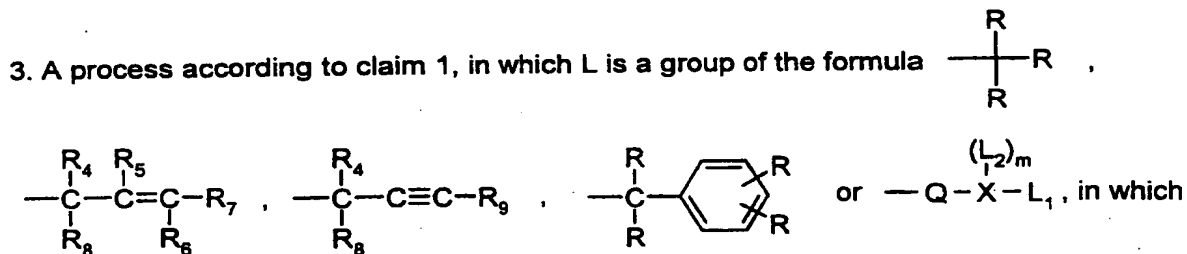
in water or an organic solvent or in a single-phase mixture thereof,

b) with a solution comprising from 0.01 to 50% by weight, based on the solution, of an organic  $\text{C}_1\text{--C}_6$  carboxylic acid in water or an organic solvent or in a single-phase mixture thereof, and

c) converting the compound of the formula (I) thermally to a pigment of the formula  $A(H)_x$

(V).

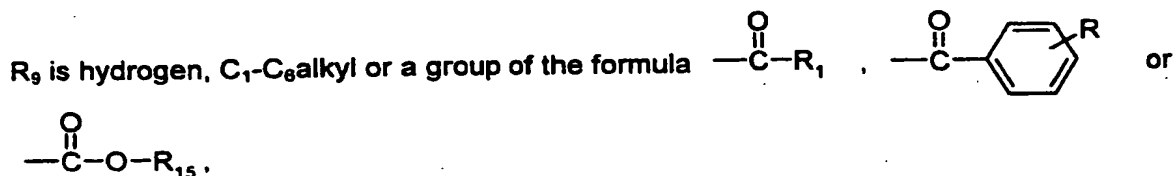
2. A process according to claim 1, wherein the pigment of the formula A(H)<sub>x</sub> (V) comprises Colour Index Pigment Yellow 13, Pigment Yellow 73, Pigment Yellow 74, Pigment Yellow 83, Pigment Yellow 93, Pigment Yellow 94, Pigment Yellow 95, Pigment Yellow 109, Pigment Yellow 110, Pigment Yellow 120, Pigment Yellow 128, Pigment Yellow 139, Pigment Yellow 151, Pigment Yellow 154, Pigment Yellow 175, Pigment Yellow 180, Pigment Yellow 181, Pigment Yellow 185, Pigment Yellow 194, Pigment Orange 31, Pigment Orange 71, Pigment Orange 73, Pigment Red 122, Pigment Red 144, Pigment Red 166, Pigment Red 184, Pigment Red 185, Pigment Red 202, Pigment Red 214, Pigment Red 220, Pigment Red 221, Pigment Red 222, Pigment Red 242, Pigment Red 248, Pigment Red 254, Pigment Red 255, Pigment Red 262, Pigment Red 264, Pigment Brown 23, Pigment Brown 41, Pigment Brown 42, Pigment Blue 25, Pigment Blue 26, Pigment Blue 60, Pigment Blue 64, Pigment Violet 19, Pigment Violet 29, Pigment Violet 32, Pigment Violet 37, 3,6-di(4'-cyano-phenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione, 3,6-di(3,4-dichlorophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione or 3-phenyl-6-(4'-tert-butylphenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.



R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> independently of one another are C<sub>1</sub>-C<sub>8</sub>alkyl,

R<sub>4</sub> and R<sub>8</sub> independently of one another are C<sub>1</sub>-C<sub>8</sub>alkyl, C<sub>1</sub>-C<sub>8</sub>alkyl interrupted by O, S or N(R<sub>12</sub>)<sub>2</sub>, or unsubstituted or C<sub>1</sub>-C<sub>8</sub>alkyl-, C<sub>1</sub>-C<sub>8</sub>alkoxy-, halogen-, cyano- or nitro-substituted phenyl or biphenyl,

R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> independently of one another are hydrogen or C<sub>1</sub>-C<sub>8</sub>alkyl,



$R_{10}$  and  $R_{11}$  independently of one another are hydrogen,  $C_1$ - $C_6$ alkyl,  $C_1$ - $C_6$ alkoxy, halogen, cyano, nitro,  $N(R_{12})_2$  or unsubstituted or halogen-, cyano-, nitro-,  $C_1$ - $C_6$ alkyl- or  $C_1$ - $C_6$ alkoxy-substituted phenyl,

$R_{12}$  and  $R_{13}$  are  $C_1$ - $C_6$ alkyl,  $R_{14}$  is hydrogen or  $C_1$ - $C_6$ alkyl and  $R_{15}$  is hydrogen,  $C_1$ - $C_6$ alkyl, unsubstituted or  $C_1$ - $C_6$ alkyl-substituted phenyl,

Q is p,q- $C_2$ - $C_6$ alkylene which is unsubstituted or substituted one or more times by  $C_1$ - $C_6$ alkoxy,  $C_1$ - $C_6$ alkythio or  $C_2$ - $C_{12}$ dialkylamino, p and q being different locants,

X is a heteroatom selected from the group consisting of N, O and S, m being 0 if x is O or S and 1 if x is N, and

$L_1$  and  $L_2$  independently of one another are  $[-(p',q'-C_2-C_6alkylene)-Z-]_n-C_1-C_6alkyl$  or  $C_1-C_6alkyl$  which is unsubstituted or substituted one or more times by  $C_1$ - $C_{12}alkoxy$ ,  $C_1$ - $C_{12}alkythio$ ,  $C_2$ - $C_{24}dialkylamino$ ,  $C_6-C_{12}aryloxy$ ,  $C_6-C_{12}arylthio$ ,  $C_7-C_{24}alkylaryl amino$  or  $C_{12}-C_{24}diaryl amino$ , n being a number from 1 to 1000, p' and q' being different locants, each Z independently of the others being a heteroatom O, S or  $C_1$ - $C_{12}alkyl$ -substituted N, and  $C_2$ - $C_6alkylene$  in the repeating units  $[-C_2-C_6alkylene-Z-]$  being identical or different,

and  $L_1$  and  $L_2$  may be saturated or unsaturated 1 to 10 times, uninterrupted or interrupted at any desired points by from 1 to 10 groups selected from the group consisting of  $-(C=O)-$  and  $-C_6H_4-$ , and  $L_1$  and  $L_2$  may carry none or from 1 to 10 further substituents selected from the group consisting of halogen, cyano and nitro.

4. A process according to claim 1, wherein the carboxylic acid comprises formic acid, acetic acid, propionic acid, pivalic acid, oxalic acid, malonic acid, succinic acid or citric acid.

5. A process according to claim 1, wherein the overall concentration of the salts of the formula (II), (III) or (IV) is from 1 to 150% by weight of the overall concentration of the compounds of the formula (I).

6. A process according to claim 1, wherein the single-phase mixture consists of from 5 to 25% by weight of water and from 95 to 75% by weight of an alcohol or ketone and the overall concentration of the salts of the formulae (II), (III) and (IV) is from 0.01 to 2% by weight, preferably from 0.05 to 0.10% by weight, based on the solution.

7. A process according to claim 1, wherein the temperature for the thermal conversion is from 40 to 160°C, preferably from 80 to 120°C.



# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/EP. 00/09376

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B27K5/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B27K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 792 357 A (BIER KURT E G) 20 December 1988 (1988-12-20) column 1, line 53 -column 2, line 6	1
A	US 4 752 297 A (LEACH ROBERT M) 21 June 1988 (1988-06-21)	
A	WO 98 58027 A (CIBA GEIGY AG) 23 December 1998 (1998-12-23) cited in the application	

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*8\* document member of the same patent family

Date of the actual completion of the international search

15 February 2001

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05/03/2001

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/09376

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